

Diffuse phase transition in ferroelectrics with mesoscopic heterogeneity: Mean-field theory

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The diffuse phase transition in ferroelectrics with mesoscopic heterogeneity has been discussed within the context of a superparaelectric model by using the Ginzburg-Landau formalism. In the Curie region ferroelectrics with mesoscopic heterogeneity are treated as "superparaelectrics" consisting of a mass of polar clusters, each of which has Ising character. Based on the mean-field theory, the influence of the finite-size effects of polar clusters on their structural instability has been discussed by considering a coherent lattice coupling between two structurally different regions. In particular, we have analytically derived the explicit solutions of the distribution of local polarizations. In turn, the processes of polar nanophase precipitation and coarsening have been also discussed in conjunction with the local chemical or structural inhomogeneity. Moreover, we have also analyzed the relationship between the local polarization distribution and the static dielectric susceptibility in ferroelectrics with the nanometric scale heterogeneity. The width of the Curie region is dependent upon the distribution of the sum of localized correlation length, which reflects the size distribution of heterogeneity. The presented analysis reveals that the diffuse phase transition is closely associated with the existence of nanometric polar clusters and their physical size distribution. Intriguingly, our theoretical results bear a very close resemblance to most experimental observations. [S0163-1829(97)03518-2]

I. INTRODUCTION

The dielectric response in ferroelectrics is mainly determined by the characteristics of transverse-optic phonons or soft modes, which virtually reflect the relative movement between cations and anions. Usually the dielectric constants in ferroelectrics can be estimated by the Lyddane-Sachs-Teller (LST) relation, or their phase transition behavior can be quite accurately described by mean-field theories, such as the Landau theory.¹ In normal ferroelectrics, as a rule, the dielectric coefficient peaks at the transition temperature T_c showing a typical Landau behavior. However, a variety of ferroelectrics, such as dielectric composites,¹⁻³ complex perovskite ferroelectrics,^{4,5} disorder or random dipole ferroelectrics,^{6,7} ferroelectrics with graded compositions,^{8,9} and even nanostructured ferroelectrics and ceramics with ultrafine grains,¹⁰⁻¹² exhibit a very broad peak near their Curie temperatures, whose dielectric coefficients often are larger than those suggested by the LST relation. The phase transitions in these materials are called as the diffuse phase transition (DPT) because they are characterized by broad anomalies in the dielectric response near transition temperature regions, resulting in an exceeding enhancement of dielectric, pyroelectric, elastic-electric, and optoelectric properties within a wide temperature range. More precisely, the principal signature of the DPT is based on the fact that the dielectric susceptibility near the Curie region is governed by the relation^{10,13,14}

$$\frac{1}{\chi} = \frac{1}{M} + \frac{(T - T_c)^\alpha}{N}, \quad 1 \leq \alpha \leq -2 \quad (1)$$

rather than the usual Curie-Weiss law obeyed by normal ferroelectrics. The coefficient α in Eq. (1) increases when the transition becomes more diffused.

In general, the common feature shared by all ferroelectrics with the DPT is that they possess compositional variations, structural inhomogeneities, or phase heterogeneities in the physical scale from micron or submicron range to the atomic level. In fact, physically the inhomogeneity within ferroelectrics influences the manner in which the materials exhibit ferroelectricity.

Experimentally it has been substantially reported that a variety of complex mixed perovskite ferroelectrics with DPT behavior, such as $\text{Pb}(\text{Mg}, \text{Nb})\text{O}_3$ (PMN), $(\text{Pb}, \text{La})(\text{Zr}, \text{Ti})\text{O}_3$ (PLZT), or $(\text{Sr}, \text{Ba})\text{Nb}_2\text{O}_6$, have a truly nanometer scale heterogeneity in composition. These types of ferroelectrics are also called ferroelectric relaxors because they also exhibit a significant dispersion of dielectric response near the Curie range, giving rise to sizable nonlinear dielectric and electromechanical phenomena.

The nature of the diffuse phase transition in ferroelectric relaxors has been a long standing puzzle since their detection nearly four decades ago. The high interest in the phase-transition behavior of ferroelectric relaxors not only resides in their fundamental significance, but also it is due to their practical importance¹⁵ because ferroelectric relaxors have the largest intrinsic dielectric constants among all materials on earth.

Forty years ago Smolenskii and co-workers^{13,16-18} provided an intuitive picture of the diffuse phase transition in complex ferroelectrics. Through the assumption of a local distribution of phase-transition points and the concept of microregion (Kanzig region), they empirically estimated the broadening of the phase transition, although they could not

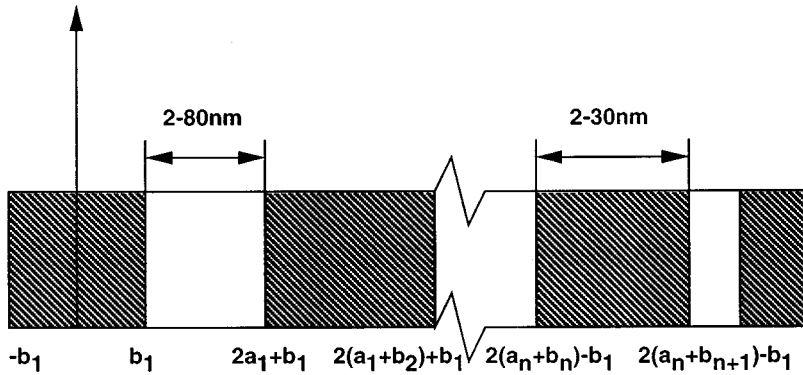


FIG. 1. Schematic representation of the distribution of local order parameters in an inhomogeneous system.

offer a solid physical ground about their assumption. Following Smolenskii's pioneer work, many important researches about ferroelectric relaxors were carried out in the 1960's–1990's, and a number of models have been proposed for interpreting the dielectric response of the relaxors. Here we do not attempt to review the enormously voluminous experimental and theoretical literature in this area. However, it should be emphasized that Cross¹⁹ proposed a superparaelectric model which suggested that the DPT in the relaxors is generated by their mesoscopic heterogeneity.

Nevertheless so far the detailed physical process of the diffuse phase transition in these materials has not been understood completely yet. Unresolved questions include, the exact nature of the diffuse phase transition and the intrinsic connection between the heterogeneity and their dielectric response. Particularly interesting is the phase-transition width or the diffuseness of the phase transition, which influences practical applications. An intriguing question here is: does the width of the Curie region really, as expected before, depend on the dipole-dipole interaction between clusters, or does another generic cause related with the microstructure itself govern the diffuseness of the phase transition? As a matter of fact, a more profound fundamental issue is: is it possible to artificially engineer and manipulate ferroelectric phase transition by controlling the mesoscopic heterogeneity in order to tailor and design dielectric properties of ferroelectric dielectrics?

It is the thesis of this paper that the origin of the diffuse phase transition in ferroelectric relaxors lies in a size effect and ties up with their heterogeneity and relevant physical scale. In this work, we attempt to quantify the correlation between the diffuse phase transition in relaxors and their mesoscopic heterogeneity, although experimentally enormous evidence has strongly suggested that the formation of polar clusters with nanometer size, on a scale significantly larger than the lattice constant, is responsible for their diffuse phase transition.¹

In light of the complexity of the topic, we have organized this paper as follows. In Sec. II, we present an extended Ginzburg-Landau model for the case of the inhomogeneous system by constructing a simple but rather realistic free-energy equation for such a system. In Sec. III, we evaluate the shift of local phase-transition points, and the explicit solutions of polarization distribution are given by a continuum theory. Section IV contains a quantitative analysis of the

features of diffuse phase transition of ferroelectric relaxors, in which we discuss the relationship between the behavior of local polarization and overall dielectric response. We calculate the temperature variation of order parameters along with the responses to a weak external field, and we show how the overall phase transition is controlled through mesoscopic heterogeneities. Finally our conclusions are summarized in Sec. V.

II. THEORETICAL ANALYSIS: FREE-ENERGY EQUATION IN A COHERENT SYSTEM

The essence of the present work, as will emerge below, is an effort to quantitatively analyze the dielectric response and the phase stability of polar clusters in relaxors in connection with their physical sizes and the features of their diffuse phase transition. One of the primary difficulties concerning DPT in relaxors is to describe spatial inhomogeneities in the system analytically. For simplicity let us first envisage an inhomogeneous system consisting of two different chemical regions. One is subsystem *A* as the matrix phase and another is denoted as subsystem *B* as illustrated in Fig. 1, each of which behaves as a “Devonshire ferroelectric.” In reality, the subsystems *A* and *B* are interconnected with one another as a 0-3 nanocomposite. To constructing an analytic expression of total free energy, we introduce two local order parameters, $P_a(r)$ and $P_b(r)$, corresponding to the polarization of subsystems *A* and *B*. Both localized order parameters together can describe the polarization behavior in a medium, i.e., an ensemble of clusters within a matrix, on the mesoscopic scale, over which there are enough atoms present so that the order parameters have thermodynamic meaning, and they can be described in the approximation of a continuous medium. In the following analysis, we restrict ourselves to the following conditions. (i) Two local scale order parameters correspond to a one-component representation, such as the case of the $\langle 111 \rangle$ direction in PMN system. The two order parameters have their intrinsic bulk Curie points when the physical sizes of two subsystems are infinitely large; and (ii) there is a direct coherent coupling between two order parameters at interfaces and the phase transition in each subsystem is of the second order. By following the free-energy expressions in the literature,^{20–23} the thermodynamic potential of an inhomogeneous system can be constructed in a Landau-Ginzburg form,

$$\Phi = \int \left\{ \Phi_{a0} + \Phi_{b0} + \frac{1}{2} \xi_1 (\nabla P_a)^2 + \frac{1}{2} \xi_2 (\nabla P_b)^2 + \frac{A}{2} P_b^2(r) + \frac{B}{4} P_b^4(r) + \frac{C}{6} P_b^6 + \frac{\alpha}{2} P_{pa}^2(r) + \frac{\beta}{4} P_a^4(r) + \frac{\gamma}{6} P_a^6(r) \right. \\ \left. + \frac{Q_2}{2} P_b^2 \delta \left(r \pm b_{n+1} + \left[\sum_n 2n(a_n + b_n) - b_1 + b_{n+1} \right] \right) + \frac{Q_1}{2} P_a^2 \delta \left(r \pm a_{n+1} + \left[\sum_n 2n(a_n + b_{n+1}) - b_1 + a_{n+1} \right] \right) \right\} dr, \\ n=0; \pm 1; \pm 2; \pm 3; \dots, \quad (2)$$

where Φ_{a0} and Φ_{b0} denote the thermodynamic potential of subsystems A and B in the paraelectric phase state. $\alpha, \beta, \gamma, A, B,$ and C are coefficients in the thermodynamic expansion, and especially $\alpha = \alpha_0(T - T_1)$, and $A = A_0(T - T_2)$. T_1 and T_2 are the bulk phase transition temperatures in each subsystem, respectively. $T_2 > T_1$ is defined in the following discussion. ξ_1 and ξ_2 are the coefficients of gradient terms of order parameters. The Ginzburg term $\xi_i(\nabla P_i)$ reflects the presence of polarization inhomogeneities in the material. $\delta(r)$ is a delta function which describes the coordinates of the interface between two subsystems. The δ function is commonly used to represent the coupling terms at the interface in ferroelectric media.^{7,23–25} Although, in principle, the general conclusion of our theoretical results will not be affected by choosing the δ function as a connection function, it simplifies the analytical and numerical calculations.

The integral of Eq. (2) is over all space since the order parameters vary spatially. Thus, the local order parameters $P_a(r)$ and $P_b(r)$ are the functions of space coordinates. a_n and b_n are the radius of domains of subsystems in one of their polar axes. More precisely, b_n is defined as the size of subsystem B , representing high-temperature ordered clusters within ferroelectric relaxors, which is on a mesoscopic scale, i.e., $b_n = 2 - 30$ nm. The matrix phase is in fact a three-dimensional network, and the dimensional scale of the matrix phase A , a_n essentially stands for the minimum distance between two clusters, which ranges around 2 to 80 nm, from a nanometer size up to a submicron level. In reality the average size of a_n is relatively larger than b_n . The two order parameters which appear in the invariant free-energy function can possess different sequences of irreducible representations of symmetry groups in the certain temperature range. Q_1 and Q_2 are defined as the coherent coupling coefficients, which characterize the coherent coupling at the interfaces between different regions. Physically the coupling terms can be related to the stored elastic and electrostatic energy caused by coherency coupling. The coefficients Q_1 and Q_2 structurally allow the polar cluster to coherently conjugate to the other local order parameter. The spatial distribution of the polarization can be obtained by solving the Euler-Lagrange equations

$$\xi_1 \frac{d^2 P_a}{dr^2} - (\alpha P_a + \beta P_a^3 + \gamma P_a^5) = 0, \quad (3a)$$

$$\xi_2 \frac{d^2 P_b}{dr^2} - (A P_b + B P_b^3 + C P_b^5) = 0, \quad (3b)$$

with associated periodic boundary conditions

$$\left[\xi_1 \frac{dP_a}{dr} + Q_1 P_a \right] \delta P_a \Big|_{r=\Sigma_n 2(a_n + b_n) - b_1} = 0, \quad (4a)$$

$$\left[\xi_1 \frac{dP_a}{dr} - Q_1 P_a \right] \delta P_a \Big|_{r=\Sigma_n 2(a_n + b_{n+1}) - b_1} = 0, \quad (4b)$$

$$\left[\xi_2 \frac{dP_b}{dr} + Q_2 P_b \right] \delta P_b \Big|_{r=\Sigma_n 2(a_n + b_{n+1}) - b_1} = 0, \quad (4c)$$

$$\left[\xi_2 \frac{dP_b}{dr} - Q_2 P_b \right] \delta P_b \Big|_{r=\Sigma_n 2(a_n + b_n) - b_1} = 0. \quad (4d)$$

Equations (3) and (4) are obtained by functional differentiation of Eq. (2). If there does not exist a mutual coupling at interfaces between two subsystems, the thermodynamic behavior of each subsystem will become independent of each other. And then these equations would be exactly identical with those in the model of Tilley and Zeks^{21,22} for describing the behavior of finite ferroelectric systems.

By considering the interactions between two subsystems, a coherent interface state is assumed to be present at the boundaries of two subsystems. The coherency is defined by the requirement that the local order parameters from one subsystem to another subsystem are continuous across all interfaces. In this case, the order parameter in one subsystem will appear as the exact same as the order parameter of the second subsystem at interfaces, i.e.,

$$P_a(r) \Big|_{r=\Sigma_n 2(a_n + b_{n+1}) - b_1} = P_b(r) \Big|_{r=\Sigma_n 2(a_n + b_{n+1}) - b_1}, \quad (5a)$$

$$P_a(r) \Big|_{r=\Sigma_n 2(a_n + b_n) - b_1} = P_b(r) \Big|_{r=\Sigma_n 2(a_{n+1} + b_{n+1}) - b_1}. \quad (5b)$$

Accordingly Eqs. (5) become

$$\frac{dP_b}{dr} - \frac{P_b}{d_2} \Big|_{r=\Sigma_n 2(a_n + b_n) - b_1} = 0, \quad (6)$$

$$\frac{dP_b}{dr} + \frac{P_b}{d_2} \Big|_{r=\Sigma_n 2(a_n + b_{n+1}) - b_1} = 0, \quad (7)$$

$$\frac{dP_a}{dr} - \frac{P_a}{d_1} \Big|_{r=\Sigma_n 2(a_n + b_{n+1}) - b_1} = 0, \quad (8)$$

$$\left. \frac{dP_a}{dr} + \frac{P_a}{d_1} \right|_{r=\sum_n^2(a_{n+1}+b_{n+1})-b_1} = 0, \quad (9)$$

$$\text{with the condition } d = -d_1 = d_2. \quad (10)$$

Here $Q_1 = \xi_1/d_1$ and $Q_2 = \xi_2/d_2$. d_1 and d_2 are defined as the extrapolation lengths, which reflect the strength of the coherent coupling at interfaces. Conceptually d is similar to the extrapolation length in the case of an isolated small particle,²¹ measuring the strength of the surface effect. We will discuss this aspect in detail later on.

One of the implications in Eqs. (5)–(10) is that localized phonon modes in adjacent chemically different regions can be coupled to one another via an interface coupling. The polar clusters might create highly nonlocalized electric and strain fields at interfaces, and these fields might be conjugated to the other local order parameter in the vicinity of interfaces. Two points should be stressed here. (a) The coherent coupling resulting in a mutual interaction at interfaces is arising from matching the cluster phase with the parent phase at interfaces, which leads to minimizing the interfacial energy. Interfacial energy can be elastic or electrostatic in nature. (b) In reality, the interfaces between two chemically different regions are quite fuzzy. In the continuous-medium approximation it is difficult to describe the immediate vicinity of the interface boundary between two structurally different regions explicitly. However, the main concern regarding the imposed boundary conditions is only to ensure that the order parameters match exactly at the interface, other than the exact location of the interface.

III. LOCAL POLARIZATION AND LOCAL PHASE TRANSITION

A. Local polarization distribution

We next examine the influence of heterogeneity on the distribution of local polarizations. The explicit nontrivial solutions of Eqs. (3), i.e., spatial distribution of polarization $P_a(r)$ and $P_b(r)$, can be obtained precisely with the help of Eqs. (5)–(10), although, in general, they are quite cumbersome.²⁶ Specifying a chosen area $(-b_n, 2a_n + b_n)$, we now find the space profile of the local order parameter analytically. Focusing attention on the temperature region from $T_1 \leq T$, we consider that the induced local polarization $P_a(r)$ in subsystem A is small, while in subsystem B the polarization P_b deviates from P_{0b} , i.e., $P_b = (P_{b0} - \Delta P_b)$. P_{b0} is the polarization at the coordinate origin. ΔP_b is the polarization variant, primarily due to the size effect and interface interactions. By assuming $\Delta P_b/P_{b0} < 1$ if the physical dimension of b is small enough, Eqs. (3) can be approximately written as

$$\xi_2 \nabla^2 P_b = (A + BP_{0b}^2 + CP_{0b}^4) P_b, \quad P_b \in (-b_n, b_n); \quad (11a)$$

$$\xi_1 \nabla^2 P_a = \alpha P_a, \quad P_a \in (b_n, 2a_n + b_n). \quad (11b)$$

Note that the validity of the solution of Eq. (11a) can be inspected by integrating Eq. (3a) with additional symmetric boundary conditions $dP_b/dr \rightarrow 0$ and $P_b \rightarrow P_{0b}$ as $r \rightarrow 0$.

From the coherent boundary conditions of Eqs. (5), the special solutions for Eq. (11) can be approximately written as

$$P_b = P_{b0} \cos(k_2 r), \quad P \in (-b_n, b_n), \quad (12a)$$

$$P_a = \frac{P_{b0} \cos(\kappa_2 b_n)}{\cosh(k_1 a_n)} \cosh\{k_1 [r - (a_n + b_n)]\},$$

$$P_a \in (b_n, 2a_n + b_n), \quad (12b)$$

with

$$\kappa_1^2 = \frac{\alpha_0(T - T_1)}{\xi_1}, \quad (12c)$$

$$P_{b0} \pm \left\{ -\frac{B}{2C} \left[1 - \sqrt{1 - \frac{4A_0 C}{B^2} (T - T_{2c})} \right] \right\}^{1/2},$$

and

$$T_{2c} = T_2 - (\xi_2 \kappa_2^2 / A_0), \quad (12d)$$

where κ_1 and κ_2 are defined as the characteristic lengths, which reflect the correlation radius of the order parameters and describe the breath of polarization fluctuation in each subsystem. Inserting Eq. (12b) into Eqs. (8) or (9), one obtains

$$\kappa_1 \tanh(\kappa_1 a_n) = \frac{1}{d}. \quad (13)$$

Since $T \gg T_1$ and thus $\kappa_1 a_n \gg 1$, one further has

$$\kappa_1 = \frac{1}{d}. \quad (14)$$

Equation (14) implies that the extrapolation length of d in this case is associated with the physical properties of the adjacent phase and temperature as well. On the contrary, in the situation of free surfaces (air-solid interface), the extrapolation length of an isolated nanometric particle can be mainly considered as a constant.^{21,22} This argument in fact makes sense by considering the fact that the coherent coupling strength at solid-solid interfaces should be closely associated with the surrounding interfacial environment or the feature of lattice vibrations in the adjacent phase. Likewise, inserting Eq. (12a) into Eqs. (6) or (7), one has

$$\tan(\kappa_2 b_n) = \frac{1}{\kappa_2 d}. \quad (15)$$

When the physical size of polar cluster b_n is small, the term $\tan(\kappa_2 b_n)$ in Eq. (15) can be expanded as a Taylor series. By neglecting the higher-order terms of $(\kappa_2 b_n)$ in Eq. (15) and using Eq. (14), Eq. (12d) will become

$$T_{2c} = T_2 - (\xi_2 \sqrt{|\alpha|} / \sqrt{\xi_1} b_n A_0). \quad (16a)$$

Equation (16a) can approximately estimate the shift of the Curie point in the cluster phase B . Clearly, the original Curie transition points are modified by the physical size and the coherent coupling strength. Figure 2 shows the transition temperature dependence of the physical size b_n of nanomet-

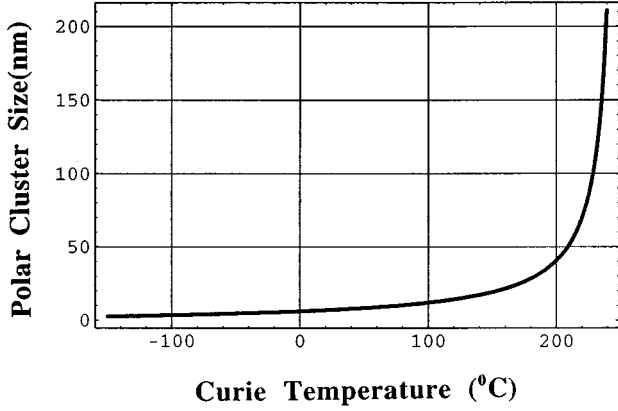


FIG. 2. The physical sizes of polar clusters as a function of their size-induced phase transition point. The free-energy parameters for this calculation can be found in Tables I and II, which have the cgs unit unless specified.

ric clusters. Essentially the phonon modes of one region can couple to the soft mode in the adjacent region locally to perturb the stability of polar phase and soft-mode transition, giving rise to a disturbance of the correlation of dipoles, and thus leading to a shift of the Curie temperature.

On the other hand, when temperature is below or near to T_1 , the polarization variant ΔP_b in the cluster domain becomes negligibly small. And then from Eqs. (3) and (10), the shift of the Curie point of the matrix phase A near interfaces can be also estimated by

$$T_{1c} = T_1 + (\xi_1 \sqrt{|A|} / \sqrt{\xi_2 a_n \alpha_0}). \quad (16b)$$

The underlying physics here is that two local order parameters are reconciled by a coherent interface boundary condition. The coherent coupling between these order parameters influences the softening of local phonon modes, leading to a shifting of the Curie temperatures of both the nanometric cluster phase and the matrix phase, respectively.

The variations of polarization in polar clusters are plotted as the functions of temperature and their physical size in Fig. 3. The induced polarization P_a in subsystem A is also numerically plotted as the functions of both the normalized

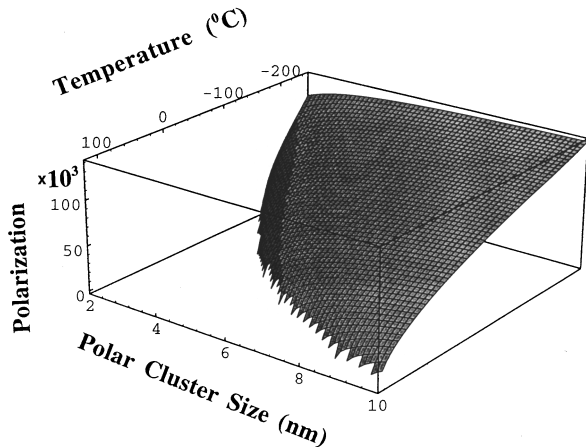
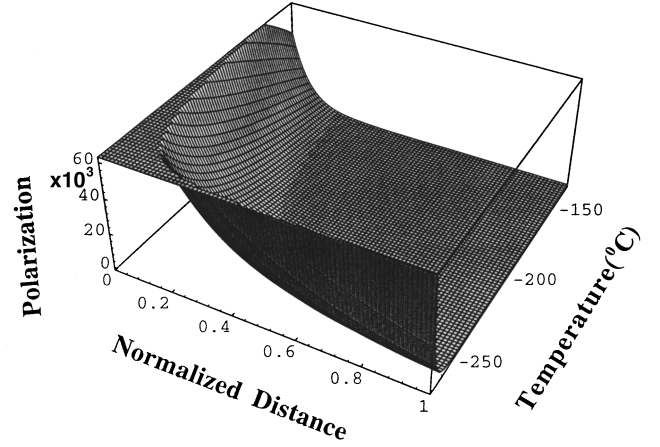
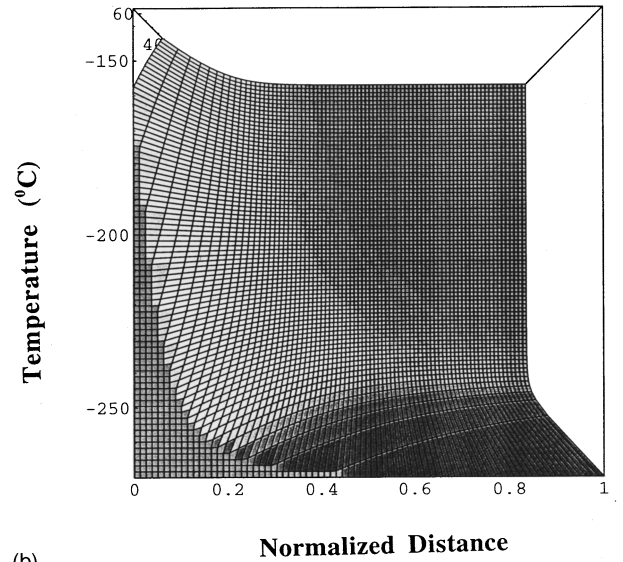


FIG. 3. Calculated polarization of a polar cluster as functions of both temperature and its physical size.



(a)



(b)

FIG. 4. Different views of the induced polarization at the interface. The normalized distance stands for $(r-b_n)/b_n$. b_n is the physical size of polar clusters and we take $b_n=5$ nm here for the calculation. (a) The spatial profile of induced polarization in the matrix as a function of temperature and the normalized distance. (b) The local transition temperature is defined as one at which the induced polarization approaches zero, i.e., $P_a=0$. The distribution of the local Curie temperatures in subsystem A near the interface is illustrated here.

coordinate and temperature in Figs. 4. It can be seen that the polarization in polar clusters P_b decreases at interfaces, while induced polarization P_a increases near interfaces. Several important features are apparent: (i) The cluster phase B can induce the polarization in the periphery of subsystem A , even though the temperature is above the original local Curie temperature of subsystem A . In other words, a polarization $P_a(r)$ occurring in subsystem A is caused by the coherent coupling from subsystem B . (ii) The initial size of a polarized cluster is determined by the spatial inhomogeneity. As the temperature decreases, the size of the polarized regions will grow, forming a polar nanodomain with a size almost twice as large (8–10 nm) as the initial one (4–5 nm) at low temperature. The temperature evolution of the spatial

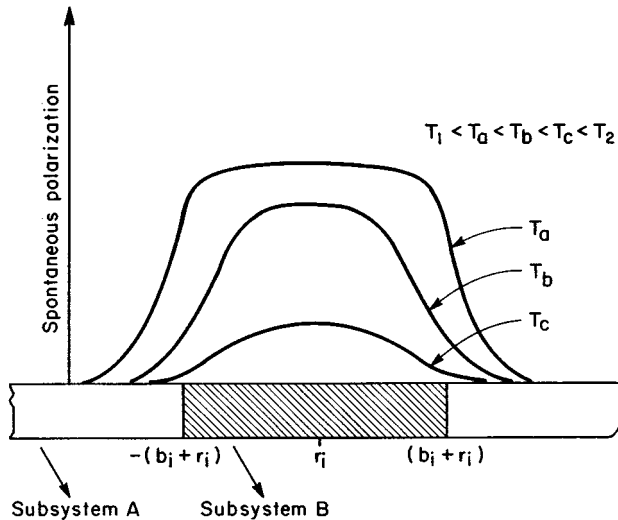


FIG. 5. Illustration of the growth pattern of polar clusters by the polarization spatial profile at different temperatures.

profile of a cluster polarization is schematically depicted in Fig. 5. It is clear that upon cooling the region near the boundary between two subsystems can no longer sustain a structure with zero polarization, even within subsystem A. As expected, the ferroelectric phase transition can be nucleated in this region, even though this region is intrinsically the paraelectric phase. The polarization occurring in subsystem A is extrinsic in nature at this temperature stage. Experimentally the growth of polar microregions in PLZT and other relaxors has been observed as temperature decreases,²⁷⁻²⁹ which is quite consistent with our theoretical description. From the lattice vibration point of view, the two subsystems have different characteristics of phonon modes because of differences in composition. The coherent coupling can link two local order parameters coherently and influences the softening of the local phonon modes upon one another in some degree.

B. Local phase transition

We now look at the distribution of local Curie temperatures at interfaces. Figure 4(a) shows that as the boundary between polar cluster and nonpolar matrix moves into sub-

system A, the size of polarized region increases. If we define the local Curie temperature as the point at which the local spontaneous polarization just approaches zero, one can find in Fig. 4(b) that the local Curie temperature will drop rapidly from the periphery of subsystem A to the interior of subsystem A where the chemical composition favors an unpolarized state in this temperature range. Quite clearly, at the exact interface, the local Curie point is the transition temperature of polar clusters, and then it decreases quickly as a function of the space coordinates.¹⁹ The essential point here is that the coupling-induced polar structure in a paraelectric matrix phase can exist even above its intrinsic Curie temperature. The local Gibbs free energy in subsystem A as a function of space-polarization coordinate can be obtained by substituting Eq. (12b) into Eq. (2), as illustrated in Fig. 6. The evolution of potential wells represents the magnitude of induced polarization in subsystem A.

Lastly, we close this section by making some comments on the coherent coupling and the range of applicability of the Landau theory. The so-called coherent coupling between two localized order parameters means that discontinuities in the distribution of order parameters are not permitted along interfaces. The lattice coupling plays an important role in the coherent coexistence of two phases with slightly different lattice parameters and symmetry. There are two fundamental reasons why the coherent coupling would occur in real systems. Since incoherent interfaces usually have higher interfacial energies than coherent interfaces, the coherent equilibrium at the interfaces is actually the stable state if the lattice match is close enough.^{30,31}

On the other hand, in its main approximation, the Landau theory of phase transitions ignores long-wave fluctuations of order parameters. However, it is important to realize that one can calculate contributions from the long-wave fluctuations as long as the contributions are small enough.³²⁻³⁶ The critical range is proven to be very narrow in ferroelectrics³²⁻³⁴ because the smoothly varying Coulomb force is responsible for establishing the polar phase. In fact, the logarithmic corrections have been proven to be difficult to detect experimentally. In experiments, the observed phase-transition behavior generally appears in agreement with the results of Landau theory. Practically, in most of cases, one can use the Landau theory to describe the phase transition for the entire phase-transition region. Therefore, it appears safe to assume that

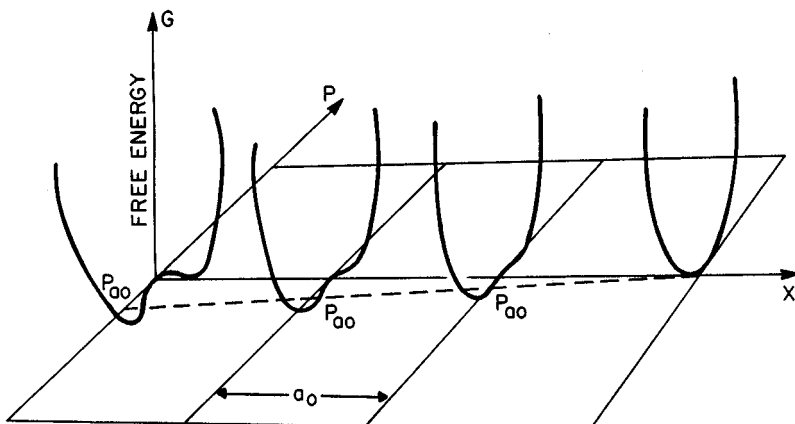


FIG. 6. The local Gibbs free energy in subsystem A as a function of the distance away from the interface at 40 K. The scale of a_0 is in range of 1 nm.

Landau theory will describe the principal physical features of polarization processes in this study.

IV. DIFFUSE PHASE TRANSITION

Next we explore the connection between the nature of diffuse phase transformation and the compositional inhomogeneity. One of the important properties for ferroelectric re-

laxors is their mean static susceptibility $\chi(T)$ near the Curie range. The static susceptibility of ferroelectrics is defined as

$$\chi_i = \left. \frac{\partial P_i}{\partial E} \right|_{E=0} = \left[\frac{\partial^2 \Phi}{\partial P_i^2} \right]^{-1} \quad (i = a, b). \quad (17)$$

Varying the total free energy of Eq. (2) with respect to P , one can obtain a variation equation,

$$\begin{aligned} \hat{\delta}\Phi = & \sum_n \int_{-r_{1n}}^{r_{1n}} \{ [AP_b + BP_b^3 + CP_b^5 + Q_2 P_b \delta(r \pm r_{1n})] \hat{\delta}P_b + \xi_2(\nabla P_b) \hat{\delta}(\nabla P_b) \} dr \\ & + \int_{-r_{2n}}^{r_{2n}} \{ [\alpha P_a + \beta P_a^3 + \gamma P_a^5 + Q_1 \delta(r \pm r_{2n})] \hat{\delta}P_a + \xi_1(\nabla P_a) \hat{\delta}(\nabla P_a) \} dr, \end{aligned} \quad (18)$$

where

$$r_{1n} = b_{n+1} + \sum 2(a_n + b_{n+1}) - b_1 + b_{n+1} \quad \text{and} \quad r_{2n} = a_{n+1} + \sum 2(a_n + b_{n+1}) - b_1 + a_{n+1}.$$

With the help of the integral formula

$$\int_{-r_{in}}^{r_{in}} \{ \xi_i(\nabla P_i) \hat{\delta}(\nabla P_i) \} dr = \xi_i(\nabla P_i) \hat{\delta}P_i \Big|_{-r_{in}}^{r_{in}} - \int_{-r_{in}}^{r_{in}} \{ \xi_i(\nabla P_i) \hat{\delta}(\nabla P_i) \} dr, \quad (i = 1, 2) \quad (19)$$

Eq. (18) gives

$$\begin{aligned} \hat{\delta}\Phi = & \sum_n \int_{-r_{1n}}^{r_{1n}} \{ -\xi_2(\nabla^2 P_b) + AP_b + BP_b^3 + CP_b^5 + [\pm \xi_2(\nabla P_b) + Q_2 P_b] \delta(r \pm r_{1n}) \} \hat{\delta}P_b dr \\ & + \int_{-r_{2n}}^{r_{2n}} \{ -\xi_1(\nabla^2 P_a) + \alpha P_a + \beta P_a^3 + \gamma P_a^5 + [\pm \xi_1(\nabla P_a) + Q_1 P_a] \delta(r \pm r_{2n}) \} \hat{\delta}P_a dr. \end{aligned} \quad (20)$$

Therefore, the average local inverse susceptibilities of polar clusters and the nearby matrix phase can be expressed as

$$\langle \chi_{bn}^{-1} \rangle = \frac{1}{2b_n} \int_{-r_{1n}}^{r_{1n}} \{ A + 3BP_b^2 + 5CP_b^4 + Q_2 \delta(r \pm r_{1n}) \} dr, \quad (21a)$$

$$\langle \chi_{an}^{-1} \rangle = \frac{1}{2a_n} \int_{-r_{2n}}^{r_{2n}} \{ \alpha + 3\beta P_a^2 + 5\gamma P_a^4 + Q_1 \delta(r \pm r_{2n}) \} dr, \quad (21b)$$

respectively. The identical equation

$$\int dr \{ \partial^2(\nabla P_i)^2 / \partial P_i^2 \} \equiv 0, \quad (22)$$

is used for derivation of Eqs. (21). As a straightforward consequence of Eqs. (21), the *average* susceptibility of matrix and local susceptibilities of clusters can be written as

$$\langle \chi_{a_n}^- \rangle \approx \frac{1}{\alpha_0(T - T_{1c})} \quad T > T_{1c}, \quad (23a)$$

$$\langle \chi_{a_n}^- \rangle \approx \frac{1}{-2\alpha_0(T - T_{1c})} \quad T < T_{1c}, \quad (23b)$$

$$\langle \chi_{bn} \rangle = \frac{1}{A_0(T - T_{2c}^n)} \quad T > T_{2c}^n, \quad (23c)$$

$$\langle \chi_{bn} \rangle = \frac{1}{-2A_0(T - T_{2c}^n)} \quad T < T_{2c}^n, \quad (23d)$$

with

$$\begin{aligned} T_{1n} &= T_1 + (\xi_1 \sqrt{|A|} / \sqrt{\xi_2} \alpha_0 \bar{a}_n), \\ T_{2c}^n &= T_2 - (\xi_2 \sqrt{|\alpha|} / \sqrt{\xi_1} A_0 b_n). \end{aligned} \quad (23e)$$

Here \bar{a}_n is the average minimum distance between clusters. Note that when the physical sizes a_n and b_n of cluster domains and matrix phase become very large, Eqs. (23) degenerate into expressions of susceptibility for normal ferroelectrics.^{37,38}

Generally the dielectric properties of dielectric composites could be estimated by an empirical relationship³⁹

$$\epsilon_{\text{tot}}^k = x \epsilon_1^k - (1 - x) \epsilon_2^k, \quad (24)$$

where ϵ_{tot} is the dielectric constant of an entire multiphase system. Essentially Eq. (24) is too crude to assess the dielectric response in ferroelectric relaxors because it neglects the fact that the impedance of polar clusters is relatively larger than that of the matrix and overlooks the microstructure details. In order to obtain a realistic dielectric response of ferro-

electric relaxors, according to a simple Maxwell-Wagner calculation from Eq. (A2) (see the Appendix) for multiphase dielectric systems, the effective mean static dielectric susceptibility of the entire system can be written as

$$\langle \chi \rangle \cong \sum_n \left[\frac{a_n \sigma_a}{b_n \sigma_b} \right]^2 f_{1n} \langle \chi_{an} \rangle + \sum_n \frac{b_n f_{2n}}{a_n} \langle \chi_{bn} \rangle, \quad (25a)$$

with

$$f_{1n} = \frac{a_n}{\sum_n 2(a_n + b_n)}, \quad \text{and} \quad f_{2n} = \frac{b_n}{\sum_n 2(a_n + b_n)}. \quad (25b)$$

Here f_{1n} is the volume fraction of the local matrix phase with a minimum distance a_n between two clusters, while f_{2n} is the volume fraction of cluster domains with a specific size b_n . For simplicity, by assuming $a_n \equiv a_{n+1}$, a conservative estimation of Eqs. (25) can be approximately obtained from Eq. (A3) as

$$\langle \chi \rangle \approx f_1 h \langle \chi_{\bar{a}_n} \rangle + \sum_n k f_{2n} \langle \chi_{bn} \rangle, \quad (26)$$

with

$$f_1 = \frac{2n\bar{a}_n}{\sum_n 2(\bar{a}_n + b_n)}, \quad k = (\bar{a}_n + b_n)/b_n, \quad \text{and} \quad h = \left(\frac{b_n \sigma_a}{\bar{a}_n \sigma_b} \right)^2.$$

Here f_1 is the total volume fraction of the matrix, h is a constant about 0.01–0.1, and k is a constant of 3–10, depending upon the ratio of \bar{a}_n/b_n and σ_a/σ_b . The actual information about f_{1n} , f_{2n} , \bar{a}_n , and b_n can be estimated directly from the microstructure characterization done by transmission-electron microscope (TEM).^{27–29,40–50}

Now we consider a PMN crystal consisting of a mass of clusters within a matrix. Based on Eq. (26), the overall dielectric response of a PMN system is calculated and is illustrated in Fig. 7. The calculated ϵ data yielded an excellent fit to the experimental data,^{13,51} showing a typical smeared dielectric response over a broad temperature range. The thermodynamic parameters used for our calculation are listed in Tables I and II. A salient feature demonstrated in Fig. 7 is that the overall dielectric behavior of the PMN is controlled by its heterogeneity. A set of localized phase transitions, arising from an intrinsic size effect, superpose together and coherently form a giant dielectric response over a very broad temperature range. The overall dielectric coefficient in this case is exceedingly larger than that suggested by the LST relation. The distribution of physical sizes of heterogeneity used in our calculation was roughly estimated from the microstructure information offered by the TEM characterization, and it is plotted in Fig. 8. The basic physical picture

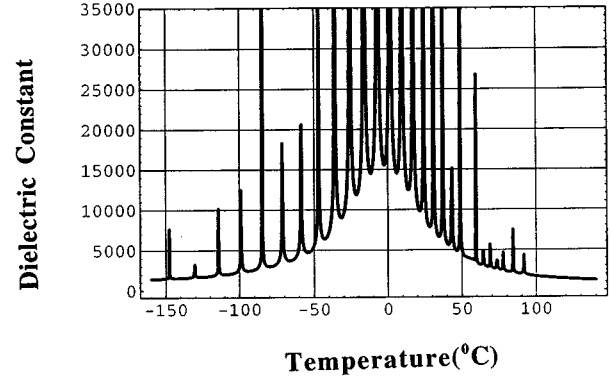


FIG. 7. The calculated temperature dependence of the mean susceptibility in a Pb(Mg,Nb) crystal.

presented in this section is straightforward: the polar phase transition tends to be confined in many localized cluster regions, ranging from a few nanometers up to more than ten nanometers, and the localized Curie points are virtually related to their physical sizes as well as the associated coherent coupling at interfaces, leading to the localized polarization fluctuation spreading over a broad temperature range. As a result, the overall phase transition will be no longer a single Curie temperature point but a continuum temperature range when the physical sizes of the polar phases form a continuum distribution.

On the other hand, the correlation lengths of localized order parameters are limited by the physical sizes of heterogeneities. The local soft modes will not propagate beyond the physical scale of the clusters. There exist a distribution of the localized correlation volumes covering a broad temperature range. It can be seen that the sum of the localized correlation volume (or length) is a function of temperature, as shown in Fig. 9, which determines the diffuseness of the Curie range in the dielectric response. In fact, a giant dielectric (pyroelectric) response is created by a set of localized dielectric singularities in a broad range of temperature.

Figure 10 shows the mean polarization of ferroelectric nanocomposite, significantly deviating from the normal ferroelectric behavior. It is found that the calculated polarization is gradually weakening and depressing, exhibiting a typical characteristic of diffuse phase-transition behavior. Quite obviously, the local polarization exists well above the temperature, at which the dielectric constant exhibits its maximum. This helps explain the experimental results that the polar regions exist well above the transition temperature, together with the absence of any evidence from x rays or neutron diffraction for a sudden structural change in going to the low-temperature phase.¹

TABLE I. Parameters of the free-energy expression for the polar clusters $\text{Pb}(\text{Mg}_{0.5}\text{Nb}_{0.5})\text{O}_3$ in PMN. Since currently there are no free-energy parameters for $\text{Pb}(\text{MgNb})\text{O}_3$ available, the free-energy parameters of $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ are adopted for our calculation [100] (cgs unit unless specified).

T_{2c}	A_0	B	C	ξ_2 (cm) ²
250 °C ^a	3×10^{-5} (Ref. 52)	0.738×10^{-12} (Ref. 52)	2.3×10^{-23} (Ref. 52)	5×10^{-16} (Ref. 53)

^a T_{2c} here is set without reference.

TABLE II. Parameters of the free-energy expression for the matrix phase in the PMN. Since currently there are no free-energy parameters for the matrix phase of $\text{Pb}(\text{Mg}, \text{Nb})\text{O}_3$ available, the free-energy parameters of SrTiO_3 are adopted for our calculation.

T_{c0}	α_0	β	γ	ξ_1 (cm) ²
35 K (Ref. 54)	1.57×10^{-4} (Ref. 55)	$4.73(T + 15.6) \times 10^{-12}$ (Ref. 54)	2.96×10^{-21} (Ref. 54)	5×10^{-16} (Ref. 53)

Equation (23e) is exactly identical with Eqs. (16). Apparently T_{1c} and T_{2c} are not only related to the physical sizes a_n and b_n of heterogeneities, but also they are associated with the elastic coefficients, and therefore their values are dependent upon a driving frequency. Qualitatively it can be seen in Eq. (23e) that T_{2c} will become larger when $|\alpha|$ gets smaller in the case of a higher driving frequency. In other words, the whole Curie range will consequently shift towards a higher temperature range under a higher driving frequency. Therefore it may be reasonably believed that significant dispersion of dielectric response near the Curie range is originated from the microstructure effect. More detailed discussions about the dynamic behavior and other aspects of ferroelectric relaxors will be discussed in several other separate papers.

In closing, we would like to make a final remark about this approach. Basically, relaxor ferroelectrics exhibit an unusual variety and richness of phase-transition features. The present approach is a quite general one, which might not explain all experimental results for all kinds of material systems in details. Nevertheless, generally, our main calculated results are consistent with the principal experimental results for some typical relaxor systems, such as PLZT(8/65/35) or $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$.

V. SUMMARY

Beginning from a basic formulation of the Ginzburg-Landau free-energy equation with physically allowed order

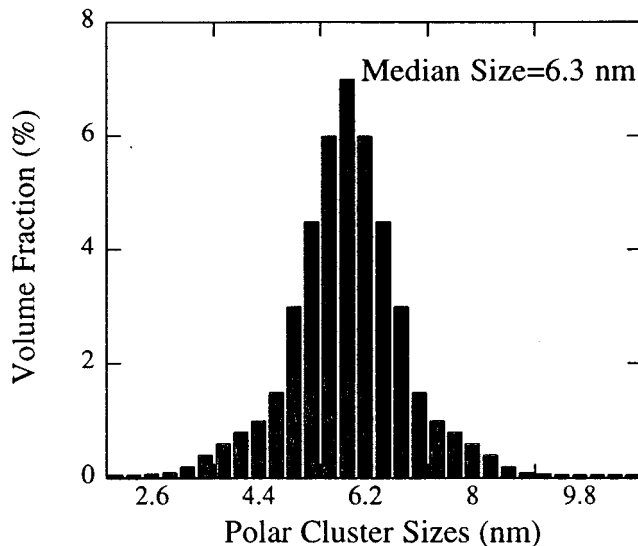


FIG. 8. The volume fraction distribution of polar clusters with different physical sizes.

parameters in an inhomogeneous medium, we have presented a straightforward thermodynamic approach to diffuse phase transitions in ferroelectrics with mesoscopic inhomogeneities. In our view, this approach provides important insights into the basic physics of the DPT in ferroelectric relaxors, and it contributes to the understanding of the structural instabilities in inhomogeneous ferroic materials. Despite a number of simplifications, the presented analysis can still explain the principal characteristics of phase transformation in ferroelectrics relaxors. Moreover, the model can account well for a number of the electrical, thermal, and microstructural observations in relaxor ferroelectrics. Next we summarize our main results.

(i) A determined effort has been made to study the dielectric behavior of a system with mesoscopic heterogeneity. The evolution of the polarization process of the coherent polar phase within a paraelectric medium has been discussed based on coherent lattice coupling and its heterogeneity. The process includes coherent precipitation and nanopolar cluster coarsening in an inhomogeneous medium. According to our model, the coherent lattice coupling between different phases imposes a critical constraint on the characteristics of local soft-mode phonons and the behavior of the phase transition in inhomogeneous media with nanopolar clusters. The local paraelectric-ferroelectric transition can be thought of as a perturbing influence of localized chemistry on localized soft-mode phonons. The unique feature in this approach is that coherent coupling is maintained across interfaces between two chemically different ordering regions.

(ii) On the basis of the spatial heterogeneity, we have

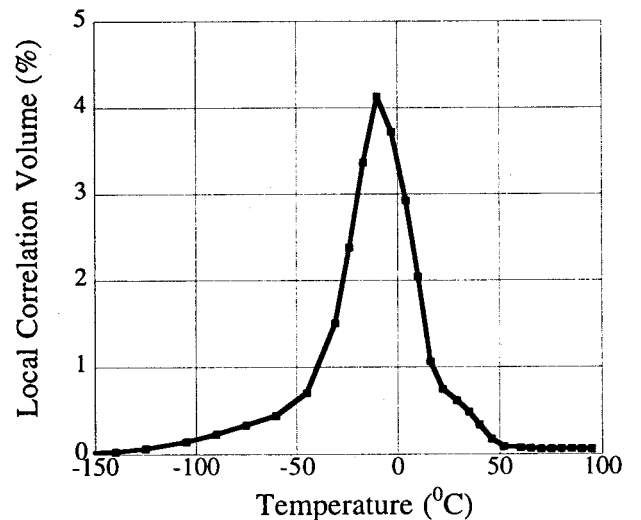


FIG. 9. The sum of the local correlation volume as a function of temperature.

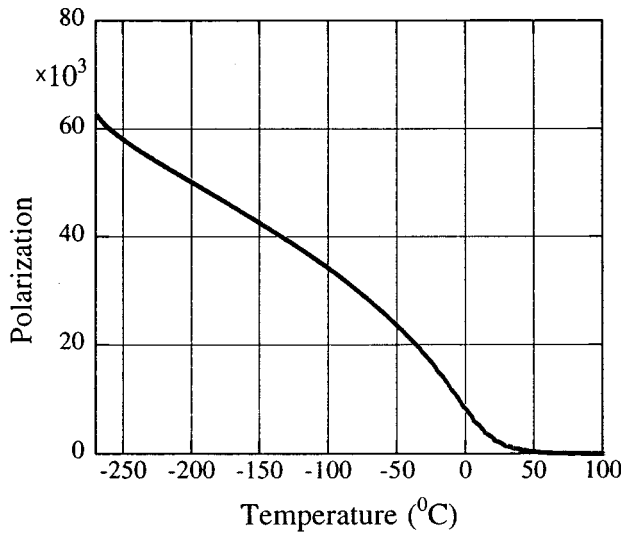


FIG. 10. The calculated temperature dependence of the mean polarization of a PMN crystal.

derived both the overall dielectric response and the local polarization distributions. We consider that each localized cluster has a mean-field character and it can be described by the Ginzburg-Landau formalism at its own “fixed point.” We connect all these localized clusters, which have size-dependent phase-transition points, to their matrix phase to describe the overall dielectric response of the entire system over a wide temperature region. Based on this approach, the diffuse phase transition in the relaxors could be understood as an inhomogeneous condensation of localized soft modes.

The analysis presented here, we believe, is the first to demonstrate how the gradual crossover characteristics of the relaxors evolve, which is inherently consistent with most of the experimental observations, and explains well the general principle of diffuse phase transition in relaxor ferroelectrics, thereby deepening our understanding of the spectacular properties of these industrially important materials.

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APPENDIX

The localized dielectric susceptibility of a cluster with a surrounding matrix layer can be estimated by a Maxwell-Wagner formalism.^{56,57} Here we take a PMN crystal as a typical example of ferroelectric relaxors with a 0–3 microstructural connection. In the cluster phase of the PMN, the Mg^{2+} and Nb^{5+} ion order is in fact in a 1:1 ratio on the *B*-site sublattice of the PMN. Since the Mg/Nb ratio is 1:1 within the ordered domains (as opposed to 1:2 for the average composition) the clusters have a net negative charge with respect to the matrix phase in order to preserve stoichiom-

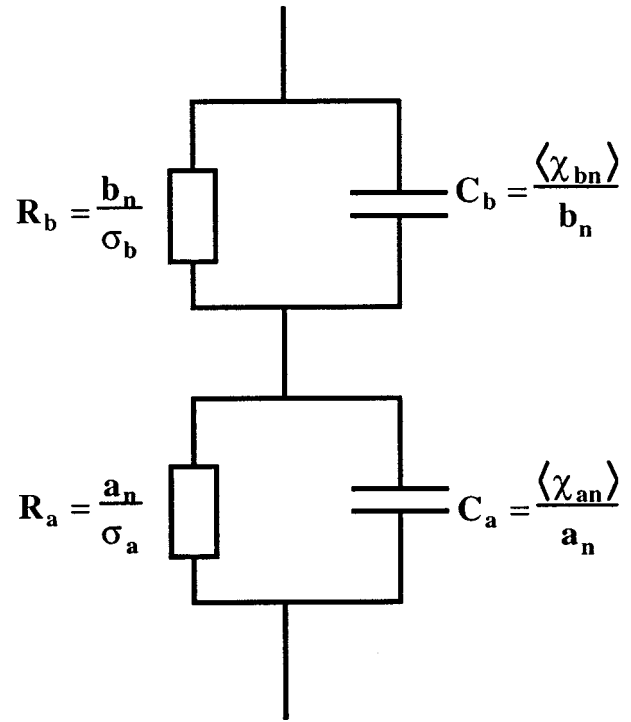


FIG. 11. Equivalent circuit diagram of a cluster with its surrounding matrix phase.

etry. It follows that the matrix must be a Mg-rich region and positively charged.

Clusters and the matrix phase can be considered as acceptor and donor-type semiconductors, respectively. The resultant pure Schottky barriers at interface boundaries between the matrix and clusters can reduce the effective conductivity of *clusters* drastically, quite analogous to the situation of a doped BaTiO_3 ceramic.^{58–60} It should be noticed that this interface effect does not essentially affect the conductivity of the matrix because its geometry connection is three-dimensional in character.

A cluster with its surrounding matrix phase can be described by an equivalent circuit as shown in Fig. 11.^{61,62} According to the equivalent circuit diagram, the local static susceptibility can be written as^{63,64}

$$\langle \chi_{1n} \rangle = \frac{(b_n \langle \chi_{bn} \rangle \sigma_a^2 + a_n \langle \chi_{an} \rangle \sigma_b^2)(b_n + a_n)}{(b_n \sigma_a + a_n \sigma_b)^2}. \quad (\text{A1})$$

Here $\langle \chi_{1n} \rangle$ is the localized susceptibility and \bar{a}_n is the average minimum size between two clusters. By considering that the effective conductivity of the cluster phase is much smaller than that of the matrix phase, $\sigma_b \ll \sigma_a$ near the cluster phase transition, the static localized susceptibility in whole temperature range can be written as

$$\langle \chi_{1n} \rangle \cong \frac{(a_n + b_n)}{b_n} \langle \chi_{bn} \rangle + \left(\frac{b_n \sigma_a}{a_n \sigma_b} \right)^2 \langle \chi_{an} \rangle. \quad (\text{A2})$$

Equation (A2) shows an interesting reverse effect of the barrier layer capacitors, similar to that of the well-known conventional interfacial capacitors,^{65,66} leading to significant enhancement of local effective dielectric properties. A quite

conservative estimation of Eq. (A2) can be obtained by assuming $\bar{a}_n \approx b_n$ and $10\sigma_a = \sigma_b$, i.e.,

$$\langle \chi_{1n} \rangle \approx 2\langle \chi_{bn} \rangle + 0.04\langle \chi_{an} \rangle. \quad (\text{A3})$$

At the optical frequency, the localized susceptibility in the whole temperature range can be written as

$$\langle \chi_{1n} \rangle = \frac{(a_n + b_n)\langle \chi_{an} \rangle}{(a_n + b_n\langle \chi_{an} \rangle / \langle \chi_{bn} \rangle)} + \frac{(a_n + b_n)\langle \chi_{bn} \rangle}{(b_n + a_n\langle \chi_{bn} \rangle / \langle \chi_{an} \rangle)}. \quad (\text{A4})$$

Equation (A4) implies that the dielectric constant of ferroelectric relaxors will be reduced at least as much as 50% when the driving frequency increases to an optical frequency level.

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